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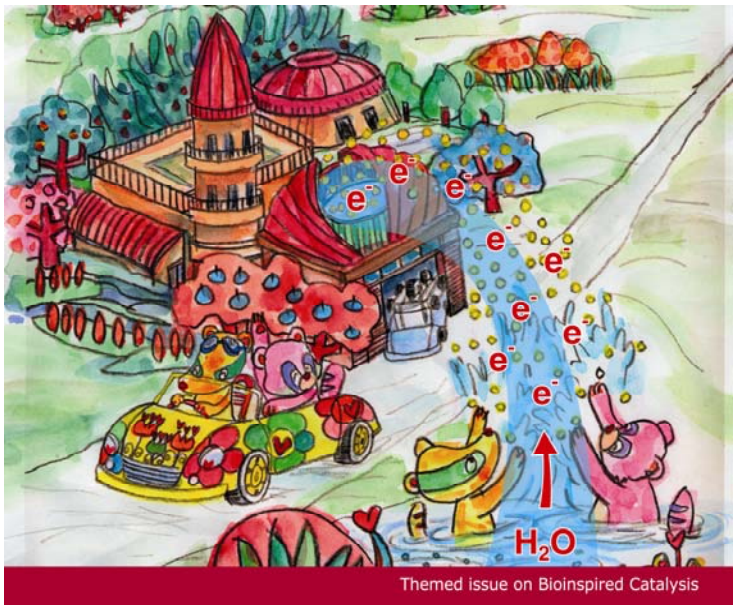

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Heterolytic H_2 activation by rhodium thiolato complexes bearing the hydrotris(pyrazolyl)borato ligand and application to catalytic hydrogenation under mild conditions†

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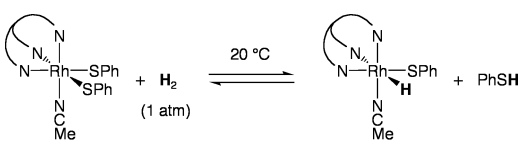
Thiolato complexes of Rh(III) bearing a hydrotris(3,5-dimethylpyrazolyl)borato ligand (Tp^{Me2}) have been prepared, and their reactivity toward H_2 has been investigated. The bis(thiolato) complex [Tp^{Me2}Rh(SPh)$_2$(MeCN)] (**1**) reacted with 1 atm H_2 at 20 °C to produce the hydrido-thiolato complex [Tp^{Me2}RhH(SPh)(MeCN)] (**2**) and PhSH *via* heterolytic cleavage of H_2. This process is reversible and in equilibrium in THF and benzene. The bis(selenolato) complex [Tp^{Me2}Rh(SePh)$_2$(MeCN)] (**4**) was also converted to [Tp^{Me2}RhH(SePh)(MeCN)] and PhSeH under 1 atm H_2, but the equilibrium largely shifted to **4**. Reaction of the dithiolato complex [Tp^{Me2}Rh(bdt)(MeCN)] (**3**; bdt = 1,2-$C_6H_4S_2$) with H_2 occurred in the presence of amine, giving the anionic hydrido complex [Tp^{Me2}RhH(bdt)]$^-$ and an equimolar amount of ammonium cations. Catalytic activity for hydrogenation has been examined under 1 atm H_2 at 20–50 °C. While **1**, **2**, and **4** slowly hydrogenated styrene at similar rates at 50 °C, activities for the hydrogenation of *N*-benzylideneaniline increased in the order, **2** < **1** < **4**. Complex **3** was found to be the most active and selective catalyst for hydrogenation of imines, and thus a variety of imines were reduced at 20 °C under 1 atm H_2, with the C=C and C=O bonds in the substrate molecules completely preserved. An ionic mechanism was involved to explain such high chemoselectivity.

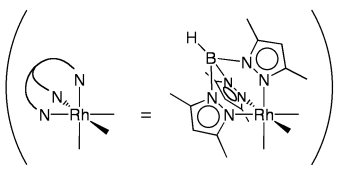
Introduction

Heterolytic activation of H_2 by transition metal complexes has been widely utilized in catalytic hydrogenation of polar bonds. Heterolysis of H_2 typically proceeds in the manner that H^+ is stripped off from the acidic H_2 ligand to leave H^- on the metal center with the assistance of an external base or an internal ancillary ligand.[1] Dihydrogen or dihydride complexes which operate by an ionic mechanism sequentially transfer H^+ followed by H^- to a substrate.[2] In well established bifunctional catalysis of chelate amido complexes, H_2 is efficiently cleaved by cooperative action of metal and amido nitrogen, forming hydride and amine hydrogen, which are then added to a substrate as H^- and H^+.[3] Hydrogen metabolism mediated by hydrogenase enzymes also involve heterolytic splitting of H_2 at the initial step.[4,5] Recent studies on [FeFe]-hydrogenase propose that the bridging dithiolato ligand in the diiron subunit contains a heteroatom (O or N) that participates in the heterolytic reactivity of H_2.[6] In the mechanism of H_2 conversion by [NiFe]-hydrogenases, it is suggested that a terminal S(Cys) moiety bound to Ni possibly accepts H^+ from the coordinated H_2.[7] Such a role of S(Cys) is also postulated in the function of [Fe]-hydrogenase, which generates H^+ and transfer H^- to an organic molecule at the monoiron site bound to cysteine residue.[8,9] As these examples in nature indicate, anionic S-donor ligands, RS^- and S^{2-}, are expected to assist heterolysis of H_2 as internal proton acceptors,[10–13] similarly to amido ligand in bifunctional catalysts. However, such a role of thiolato ligand is uncommon, and only a few of complexes have been confirmed to form M(H)–S(H)R species by the action of M–SR with H_2.[11] Consequently, reports of catalysis based on heterolytic activation of H_2 by thiolato complexes are still scarce.[12]

We have been studying transition metal thiolato complexes to develop their use in activating small molecules.[14,15] We have recently reported that the Rh(III) bis(thiolate) complex having a hydrotris(3,5-dimethylpyrazolyl)borato (Tp^{Me2}) co-ligand [Tp^{Me2}Rh(SPh)$_2$(MeCN)] (**1**) reacts reversibly with H_2 to form the hydrido–thiolato complex [Tp^{Me2}RhH(SPh)(MeCN)] (**2**) and PhSH as shown in eqn (1).[16] Based on this heterolysis of H_2, **1** showed moderate catalytic activity of hydrogenation under mild conditions. An analogous dithiolato complex [Tp^{Me2}Rh(bdt)(MeCN)] (**3**; bdt = 1,2-$C_6H_4S_2$-κ^2S,S') has turned out to be more active under ambient temperature and pressure and exclusively chemoselective to imines. We herein report a detailed study of the heterolytic activation of H_2 and catalytic hydrogenation by **1**, **3**, and analogous complexes.



(1)



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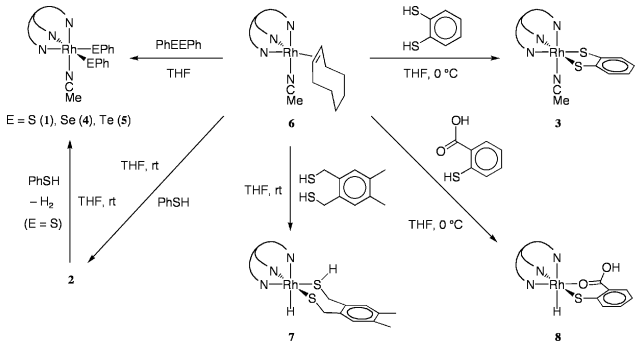
Results and discussion

Preparation and properties of bis(chalcogenolato) complexes and related compounds

The synthetic routes of the chalcogenolato complexes in this study are summarized in Scheme 1. We have previously reported that bis(benzenechalcogenolato) complexes [Tp^{Me2}Rh(EPh)$_2$(MeCN)] (E = S (**1**), Se (**4**), Te (**5**)) are prepared in good yields by the reactions of the Rh(I) complex [Tp^{Me2}Rh(cyclooctene)(MeCN)] (**6**) with 1 equiv of diphenyl dichalocogenides PhEEPh.[15a,b] It has been found that **1** is formed also from **6** and PhSH *via* the intermediate **2** with concomitant H_2 evolution.[15c] Although **6** reacts more rapidly with PhSH (60% yield of **1** after only 1 h at 20 °C) than PhSSPh (85% yield after 27 h), conversion to **1** does not complete in a closed reaction vessel due to the presence of the equilibrium shown in eqn (1).



Scheme 1

In this study, reactions of **6** were further explored with thiol compounds which could form bidentate thiolato ligands. Treatment of **6** with 1 equiv of 1,2-benzenedithiol afforded the benzenedithiolato complex [Tp^{Me2}Rh(bdt)(MeCN)] (**3**; bdt = 1,2-$C_6H_4S_2$-κ^2S,S') in moderate yield. This reaction proceeded rapidly at 0 °C with evolution of gas and, to achieve high yield, it was better to be conducted with slow evacuation. In solution, **3** was much more sensitive to O_2 than **1**, although crystals of **3** could be handled under air for a short period. The molecular structure of **3**·2THF has been determined by single crystal X-ray analysis (Fig. 1). The five-membered chelate ring constituted by the bdt ligand around the octahedral Rh(III) center is slightly bent along the S–S vector by 20° away from the Tp^{Me2} ligand. This bending is considered to be caused mainly by crystal packing, because the bent angle observed for the independently analyzed **3**·THF of the different crystal system was only 9°. The Rh–S distances at 2.3187(8) and 2.3155(9) Å are slightly shorter than those in [Tp^{Me2}Rh(SC_6H_4Me-*p*)$_2$(MeCN)] (**1′**) at 2.338(1) and 2.3420(10) Å.[15a] Other bonding parameters around the Rh center in **3** are almost comparable to those in **1′**. No significant difference is found in the C–S bond distances between **3** and **1′**.

Although the ^{1}H NMR spectra of **3** in C_6D_6 or THF-d_8 exhibited broad signals at around room temperature in contrast to **1** and other analogues, well-resolved spectra consistent with the solid-state structure were available at −20 °C in THF-d_8. On raising the temperature, the signals assignable to two inequivalent pyrazolyl groups in a ratio of 2 : 1 broadened and finally merged to one set of pyrazolyl signals. On the other hand, the ^{1}H NMR spectrum

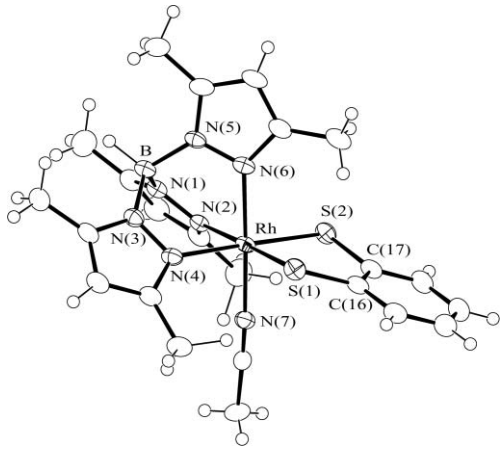


Fig. 1 ORTEP drawing of [Tp^{Me2}Rh(bdt)(MeCN)] (**3**). Solvating THF molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–S(1), 2.3187(8); Rh–S(2), 2.3155(9); Rh–N(2), 2.132(2); Rh–N(4), 2.107(2); Rh–N(6), 2.057(2); Rh–N(7), 1.998(2); S(1)–C(16), 1.765(3); S(2)–C(17), 1.765(3); S(1)–Rh–S(2), 88.16(3); S(1)–Rh–N(2), 178.76(7); S(2)–Rh–N(4), 178.08(7); N(6)–Rh–N(7), 177.26(10); Rh–S(1)–C(16), 102.47(10); Rh–S(2)–C(17), 102.76(10).

measured in CD_3CN was resolvable even at room temperature and exhibited the signal of free MeCN. These observations probably indicate that facile dissociation of the MeCN ligand and subsequent pseudo-rotation of the coordination geometry are occurring in solution. The color of the solution is orange-red in MeCN and violet in THF at room temperature, while the latter turned to orange-red at low temperature. These solvo- and thermochromic properties of **3** also support the existence of a dissociation equilibrium.

Reaction of **6** with 4,5-bis(mercaptomethyl)-*o*-xylene in THF at room temperature gave the hydrido-mercaptothiolato complex [Tp^{Me2}RhH{$SCH_2(C_6H_2Me_2)CH_2SH$-κ^2S,S'}] (**7**). The IR absorption at 2102 cm^{-1} indicates the existence of a terminal hydrido ligand. In the ^{1}H NMR spectrum measured in C_6D_6 at 50 °C, one hydrido signal appeared at δ −15.62 as a doublet with 1H intensity (J_{RhH} = 8.0 Hz). Pyrazolyl groups were observed as two sets of signals in a 2 : 1 ratio, and the signal pattern of the mercaptothiolato ligand also indicated a pseudo-C_s symmetry with respect to the plane bisecting the S–Rh–S angle. This is probably due to a rapid shift of the mercapto hydrogen between two S atoms. Although the SH group could not be confirmed by the IR spectrum, its ^{1}H signal appeared at δ 3.28. By addition of D_2O, not only this signal but also the hydrido signal disappeared at 50 °C, suggesting that the hydrido ligand was deuterated *via* exchange with the mercapto deuterium. At lower temperature, the ^{1}H NMR signals became broad and split again at −50 °C into many peaks as shown in Fig. 2. Although these signals could not be fully assigned, the presence of four major species was estimated from the spectrum of the hydrido region. The numbers of signals corresponding to Tp^{Me2} and mercaptothiolato ligands suggested that each species had a non-symmetric structure. This can be explained by the presence of conformational isomers arising from the geometry around S atoms as illustrated in Chart 1. 4,5-Bis(mercaptomethyl)-*o*-xylene reacted with **6** more slowly than 1,2-benzenethiol, probably due to the lower acidity of alkyl-SH as compared to aryl-SH, and for the same reasoning, elimination of

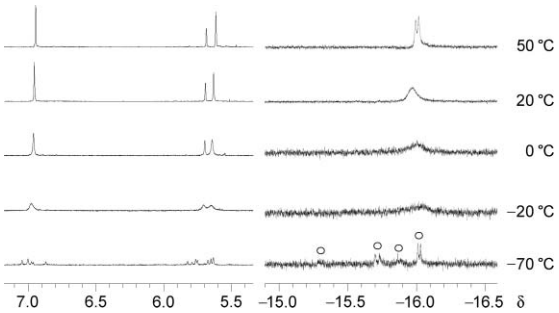


Fig. 2 VT ^{1}H NMR spectra of **7** in THF-d_8. Aromatic (left) and hydride (right) regions are shown.

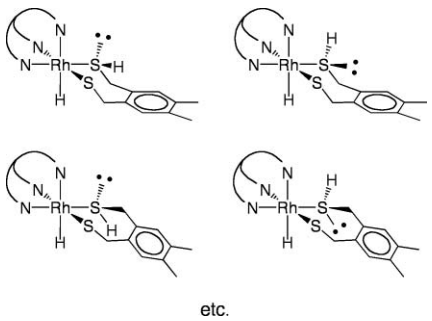


Chart 1

H_2 from the hydrido and mercapto moieties did not proceed for **7**.[17] Reaction of **6** with 1,4-butanedithiol occurred at 50 °C in THF to give a product probably analogous to **7**, although this could not be isolated. Alkanedithiols having shorter alkyl chains were found to be more reactive, but no tractable complexes were obtained.

One equiv of thiosalicylic acid reacted with **6** at 0 °C to give [Tp^{Me2}RhH(SC_6H_4-2-COOH-κ^2S,O)] (**8**) in high yield. Complex **8** was formed quite cleanly, whereas the reaction of **6** with 1 equiv of PhSH afforded a mixture of **1**, **2**, and unreacted **6**. The ^{1}H NMR spectrum of **8** showed the signals due to three inequivalent pyrazolyl groups, which were resolved well at 20 °C. Existence of one hydrido ligand was confirmed by the signal at δ −13.79 (d, $J_{RhH} = 11.6$ Hz). Although characteristic IR absorptions of neither OH nor SH could be found, the broad ^{1}H signal recorded at δ 9.13 might be assigned to the OH group rather than SH because of its highly deshielded chemical shift. This signal disappeared by addition of D_2O or Et_3N at 20 °C, while the hydrido signal was preserved. Because a low frequency shift of the C=O stretching band to 1617 cm^{-1} indicates the coordination to the Rh center, it is considered that the SC_6H_4-2-COOH ligand is bound also to the carbonyl O atom in a κ^2S,O coordination mode.

Such a structure forming a six-membered chelate-ring was confirmed by single crystal X-ray analysis (Fig. 3). The geometry of the Rh center is only slightly distorted from a regular octahedron. Fourier map indicated the existence of an hydrogen atom beside the O(2) atom, and this position was suitable to make a hydrogen bonding with a solvating THF molecule. The apparently shorter C(22)–O(1) distance than the C(22)–O(2) bond supports that the COOH group is coordinated by the C=O group. No crystallographic evidence for the SH hydrogen has been found, and the Rh–S bond is even shorter than those in other Tp^{Me2}Rh thiolato complexes, *e.g.* **1′**, **2**, and **3**. Such a coordination mode of thiosalicylate monoanion has been rarely found,[18] whilst the

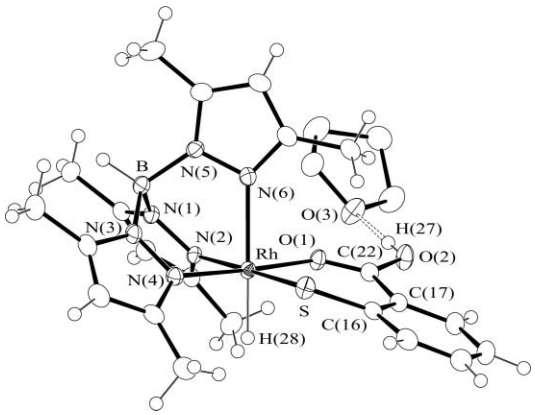


Fig. 3 ORTEP drawing of [Tp^{Me2}RhH(SC_6H_4-2-COOH-κ^2S,O)]·THF (**8**·THF). Hydrogen atoms in solvating THF molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–S, 2.2948(5); Rh–O(1), 2.044(1); Rh–N(2), 2.075(2); Rh–N(4), 2.014(2); Rh–N(6), 30.187(2); S–C(16), 1.742(2); O(1)–C(22), 1.233(2); O(2)–C(22), 1.329(2); C(17)–C(22), 1.472(2); Rh–H(28), 1.58(2); O(2)–H(27), 0.79(2); O(3)···H(27), 1.83(2); S–Rh–O(1), 92.58(3); S–Rh–N(2) 178.64(4); O(1)–Rh–N(4), 174.80(6); N(6)–Rh–H(28), 179.0(6); C(22)–O(2)–H(27), 112(2).

tautomeric *o*-C_6H_4(SH)(COO) ligand has been also reported.[19] The distances of the Rh–H bond and the elongated Rh–N bond at its *trans* position are not exceptional in comparison with previously reported values for the Tp^{Me2}Rh hydrido complexes (Rh–H, 1.44–1.49; Rh–N, 2.19–2.26 Å).[16,20]

To compare the reactivity with chalcogenolato complexes, a diiodo complex was prepared according to the method reported for Tp^{iPr2} analogue[21] and [$Tp^{Me2}RhI_2$(MeCN)] (**9**) was obtained in high yield by treatment of **6** with an equimolar amount of I_2. The molecular structure was fully determined by X-ray crystallography as depicted in Fig. 4. The Rh–N distances *trans* to the I atoms are shorter than those *trans* to the S atoms in **1′** and **3** (2.107–2.136 Å).

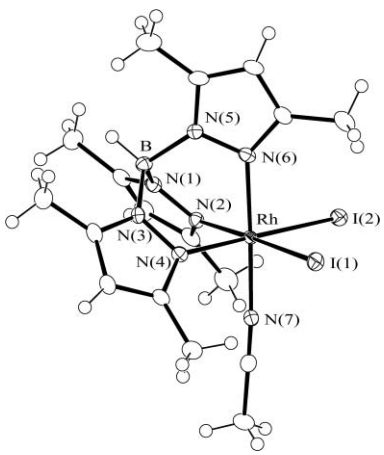


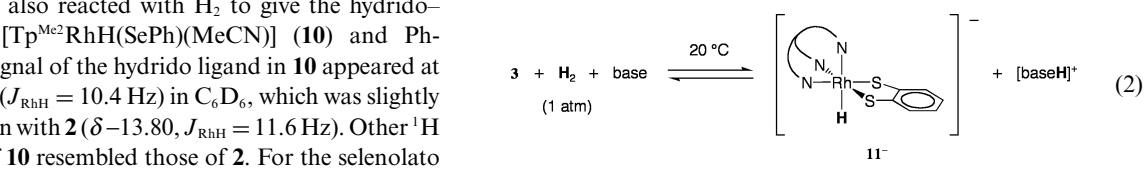
Fig. 4 ORTEP drawing of [$Tp^{Me2}RhI_2$(MeCN)] (**9**). Solvating THF molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–I(1), 2.6747(3); Rh–I(2), 2.6669(4); Rh–N(2), 2.079(3); Rh–N(4), 2.076(3); Rh–N(6), 2.055(4); Rh–N(7), 2.015(4); I(1)–Rh–I(2), 91.31(1); I(1)–Rh–N(2), 177.1(1); I(2)–Rh–N(4), 177.28(9); N(6)–Rh–N(7), 178.2(1).

Reactivities toward H_2

Reactions of the chalcogenolato complexes with H_2 were investigated using NMR. When a 10 mM solution of **1** was stirred under H_2 (1 atm) at 20 °C, the equilibrium mixtures shown in eqn (1) were obtained smoothly. The ratios of **1**:**2**:PhSH were 1 : 10 : 10 in C_6D_6 after 2 h and 1 : 14 : 14 in THF-d_8 after 1 h. When these solutions were left standing for more than 10 h, other minor species were slowly formed. When they were degassed and then kept under N_2, the amounts of **2** and PhSH gradually decreased with regeneration of **1**.

The Se analogue **4** also reacted with H_2 to give the hydrido–selenolato complex [Tp^{Me2}RhH(SePh)(MeCN)] (**10**) and PhSeH. The ^{1}H NMR signal of the hydrido ligand in **10** appeared at δ −14.05 as a doublet (J_{RhH} = 10.4 Hz) in C_6D_6, which was slightly shielded in comparison with **2** (δ −13.80, J_{RhH} = 11.6 Hz). Other ^{1}H resonance patterns of **10** resembled those of **2**. For the selenolato complexes in equilibrium, however, bis(selenolato) complex **4** is predominant as demonstrated by the ratio **4**:**10**:PhSeH of 1 : 0.60 : 0.47 in C_6D_6 after 2 h under the same conditions. It is interesting to note that the equilibrium ratio **4**:**10**:PhSeH shifts to 1 : 0.20 : 0.13 in THF-d_8 (after 2.5 h). Smaller amounts of PhSeH than **10** might indicate the formation of other species, but these could not be detected. Nevertheless, these mixtures generated under H_2 were converted back to **4** quantitatively under N_2 atmosphere after ~3 days at 20 °C. Isolation of **10** was hampered because of its low concentration in equilibrium, although the hydrido–thiolato complex **2** had been successfully crystallized under H_2.[16] Reaction of the Te congener **5** with H_2 did not proceed analogously but gave a green precipitate insoluble in common organic solvents.

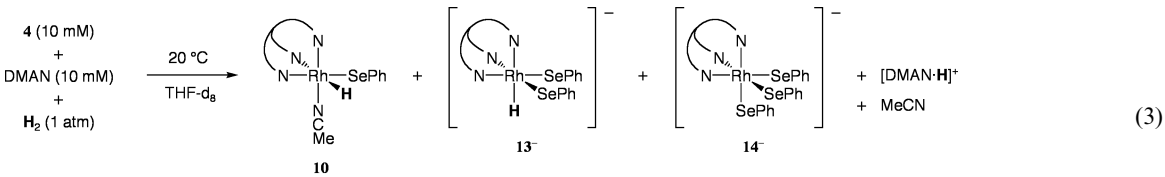
The dithiolato complex **3** in solution did not show any NMR-detectable changes under H_2 atmosphere. However, in the presence of Brønsted bases such as trialkylamines or 1,8-bis(dimethylamino)naphthalene (DMAN), the anionic hydrido complex [Tp^{Me2}RhH(bdt)]$^-$ (**11**$^-$) was generated together with a stoichiometric amount of the protonated base. The ^{1}H NMR signals of **11**$^-$ contained those of two inequivalent pyrazolyl groups in a 2 : 1 ratio, one symmetric bdt, and one hydrido ligand at δ −18.75 (d, J_{RhH} ~ 15 Hz), indicating a structure as the one depicted in eqn (2). Treatment of a THF-d_8 solution containing **3** (10 mM) and 1.2 equiv of DMAN with H_2 (1 atm) gave an equilibrium mixture of **3**, **11**$^-$, DMAN·H$^+$, and DMAN in a 65 : 35 : 33 : 87 ratio. When DMAN was replaced by 1.0 equiv of Bu_3N, the ratio of **3**:**11**$^-$ changed to 41 : 59. These equilibrium ratios are considered to be not only depending on the basicity of amines but also affected by the stability of the ion pairs. It has been discussed that the cation and anion formed from the reaction between a Brønsted acid and a base are often pairing in THF solution.[22] In this system, the ion-pair formation between **11**$^-$ and the protonated base molecule may be suggested from the NMR chemical shifts of **11**$^-$ varying significantly as the change in the counter cation (the largest $\Delta\delta$ = 0.15 between DMAN·H$^+$ and Bu_3NH^+ salts). In contrast to these reactions conducted in THF-d_8 that complete within 30 min, those in CD_3CN proceeded much more slowly. Thus, a CD_3CN solution of **3** and DMAN (each 10 mM) converted to an equilibrium mixture after 24 h, where the **3**:**11**$^-$ ratio was 26 : 74. Increase in **11**$^-$ suggests that anionic **11**$^-$ is more stabilized in polar CD_3CN than in THF-d_8, and ion-pairing seems to be loose because the NMR signals of **11**$^-$ are not affected so much by the counter cations.



(2)

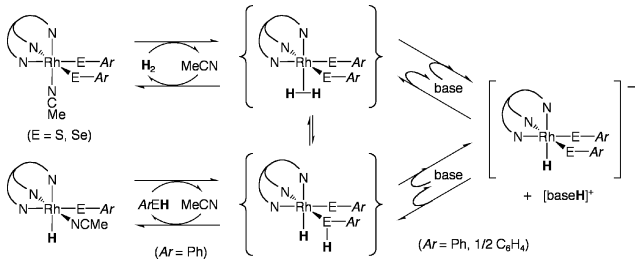
When Et_3N was added to a THF solution of **3** under H_2, precipitation of an off-white solid formulated as [Et_3NH][Tp^{Me2}RhH(bdt)] ([Et_3NH]**11**) occurred rapidly, which exhibited the ν(Rh–H) band at 2104 cm^{-1} together with the ν(N–H) band characteristic of a tertiary ammonium cation at 2670 cm^{-1} in its IR spectrum. By treating **1** with excess Et_3N in a similar manner, [Et_3NH][Tp^{Me2}RhH(SPh)$_2$] ([Et_3NH]**12**) was isolated as a yellow solid in moderate yield. While the ν(Rh–H) band of [Et_3NH]**12** appeared at 2084 cm^{-1}, its hydrido signal shifted to the lower field by ~3 ppm as compared to that of [Et_3NH]**11**. The analogous complex [Tp^{Me2}RhH(SePh)$_2$]$^-$ (**13**$^-$) was also formed by treatment of **4** with a base under H_2, but the reaction did not proceed selectively. When a THF-d_8 solution of **4** and DMAN (each 10 mM) was stirred under 1 atm H_2 at 20 °C, the product distribution converged after 9 h as shown in eqn (3). Because PhSeH was observed at the initial stage (2 h) and finally disappeared, [Tp^{Me2}Rh(SePh)$_3$]$^-$ (**14**$^-$) was formed presumably by the reaction of PhSeH and DMAN with **4**. Consumption of PhSeH in this way probably increased the ratio of **10** in comparison with the reaction without the base (*vide supra*).

These results have shown how the thiolato and selenolato complexes studied here heterolytically split the H_2 molecule into a hydrido ligand and a protic hydrogen (Scheme 2). It is plausible that these complexes interact with H_2 at the site generated by dissociation of MeCN, although the coordination equilibrium of either MeCN or η^2-H_2 is largely directed to the former. An intramolecular shift of the H atom in η^2-H_2 to the chalcogen atom forms a hydrido and a thiol (or a selenol) ligands. The following substitution of the chalcogenol ligand by MeCN leads to the hydrido–chalcogenolato complexes **2** or **10**, but this process hardly proceeds on the bidentate bdt ligand. The formation of the hydrido–thiol complex [Cp*IrH(PMe_3)(HSDmp)][BAr^F_4] (Cp* = η^5-C_5Me_5;



(3)

	4	10	13$^-$	14$^-$	DMAN	[DMAN·H]$^+$
ratio of species at equilibrium	16	33	20	31	59	49



Scheme 2

Dmp = 2,6-(mesityl)$_2$C$_6$H$_3$; Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$) from the reaction of the thiolato complex [Cp*Ir(PMe$_3$)(SDmp)][BAr$^F_4$] with H_2 has been reported.[11c] In our study, although the postulated intermediates having the η^2-H_2 ligand or the Rh(H)–E(H)R (E = S, Se) moiety were not detected for any aromatic chalcogenolato complexes, the latter structure could be seen in **7**, in which the thiolato ligands are more basic than the aliphatic ones. The other path of H_2 heterolysis is abstraction of a proton from the H_2-added complexes to leave a hydrido ligand on the metal. From our experiments, it could not be clarified whether the η^2-H_2 complex or the Rh(H)–E(H)R species is deprotonated. Since the acidity of the H_2 adduct is relatively low, an intermolecular action of Brønsted bases is necessary. Trialkylamine and DMAN had enough basicity for this process, but 2,6-lutidine and 2,4,6-colidine were not effective at all.

To evaluate the effect of chalcogenolato ligands on cleavage of H_2, the reactivity of diiodo complex **9** toward H_2 was examined, and it turned out that no reactions occur for **9** under 1 atm H_2 at 20 °C in the absence or presence of excess Et_3N. Under the same conditions, chalcogenolato complexes **1**, **3**, and **4** readily cleave the H_2 molecule. In the presence of excess Et_3N, **9** was slowly converted to [Tp^{Me2}RhHI(MeCN)] at 50 °C in THF. It has been reported that the reaction of [Tp^{Me2}RhCl$_2$(MeOH)] with Et_3N in refluxing toluene under H_2 yields [Et_3NH][Tp^{Me2}RhHCl$_2$].[23] These facts demonstrate that chalcogenolato ligands considerably reduce the activation energy in breaking H–H bond heterolytically.

Catalytic activity

It is well known that transition metal complexes that can heterolyze H_2 molecules often become effective catalysts for hydrogenation of especially polarized bonds such as C=O and C=N. Since some chalcogenolato complexes investigated here can cleave H_2 under atmospheric pressure, their catalytic activities for hydrogenation have been investigated under 1 atm H_2 to probe the feature of cleaved H atoms.

As shown in Table 1, bis(chalcogenolato) complexes **1** and **4** are found to hydrogenate styrene in moderate rates at 50 °C (entries 1–6). In contrast, bdt complex **3** is essentially inactive for hydrogenation of styrene under these conditions (entries 7, 8). Because isolated **2** shows a slightly higher activity than **1** (entry 9), the active species in C=C reduction is presumed to be the hydrido complexes related to **2**. The traditional mechanisms of hydrogenation may be adopted here: styrene is coordinated to the Rh center (probably at the site occupied by MeCN in **2**) and inserted to the Rh–H bond, and the following reaction with H_2 produces ethylbenzene and the hydrido complex. The low activity of **9** may be explained by the fact that the active hydrido complex

Table 1 Hydrogenation of styrene catalyzed by [Tp^{Me2}RhX^{1}X^2(MeCN)]

entry	catalyst (X^1; X^2)	solvent	T/°C	time/h	yield (%)[a]
1	(SPh; SPh) (**1**)	THF	20	20	16
2	(SPh; SPh) (**1**)	THF	50	10	72
3	(SPh; SPh) (**1**)	benzene	50	10	76
4	(SPh; SPh) (**1**)	EtOH	50	10	59
5	(SePh; SePh) (**4**)	THF	20	20	14
6	(SePh; SePh) (**4**)	benzene	50	16	88
7	(*o*-S$_2$C$_6$H$_4$) (**3**)	THF	50	20	1
8	(*o*-S$_2$C$_6$H$_4$) (**3**)	benzene	50	20	2
9	(H; SPh) (**2**)	THF	50	10	86
10	(I; I) (**9**)	THF	50	20	25

Conditions: styrene (1.00 mmol), catalyst (10 μmol), solvent (5 cm^3), and H_2 (1 atm).[a] Yields of ethylbenzene determined by GLC analyses.

is hardly generated under these reaction conditions for **9** (entry 10). With respect to hydrogenation of styrene, heterolysis of H_2 is a necessary step in generating active species but not involved in the catalytic cycle.

Hydrogenation of *N*-benzylideneaniline has been examined under various conditions to evaluate the activity toward imines and the results are summarized in Table 2. The activity of thiolato complex **1** toward *N*-benzylideneaniline is not high and almost similar to that toward styrene when reactions are conducted in THF (entries 1, 2), whereas selenolato complex **4** shows high activity even at 20 °C (entry 6). Interestingly, bdt complex **3** achieves hydrogenation much more rapidly at 20 °C (entry 8), and hence is exhibiting high chemoselectivity toward the C=N bond over C=C. When using **2** alone, the conversion of *N*-benzylideneaniline decreases greatly (entry 12 *vs.* 2), indicating that not only the Rh–H but also the S–H hydrogens are essential for hydrogenating the C=N bond. As predicted from the complicated or poor reactivity to H_2, **5** and **9** are not active (entries 7, 14). In addition to a drastic change in activity associated with the chalcogenolato ligands, a remarkable solvent effect has also been found. Hydrogenation of *N*-benzylideneaniline catalyzed by **1** is more accelerated in EtOH rather than in THF (entries 4, 5), but

Table 2 Hydrogenation of *N*-benzylideneaniline catalyzed by [Tp^{Me2}RhX^{1}X^2(MeCN)]

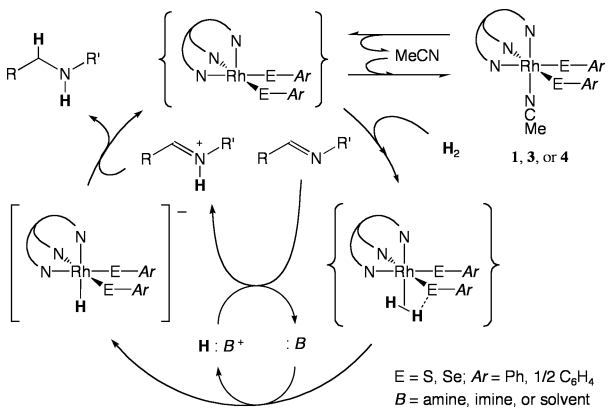
entry	catalyst (X^1; X^2)	solvent	T/°C	time/h	yield (%)[a]
1	(SPh; SPh) (**1**)	THF	20	20	21
2	(SPh; SPh) (**1**)	THF	50	10	63
3[b]	(SPh; SPh) (**1**)	benzene	50	20	5
4	(SPh; SPh) (**1**)	EtOH	20	20	32
5	(SPh; SPh) (**1**)	EtOH	50	10	99
6	(SePh; SePh) (**4**)	THF	20	6	99
7	(TePh; TePh) (**5**)	THF	50	16	22
8	(*o*-S$_2$C$_6$H$_4$) (**3**)	THF	20	1	98
9	(*o*-S$_2$C$_6$H$_4$) (**3**)	benzene	20	2	48[c]
10	(*o*-S$_2$C$_6$H$_4$) (**3**)	THF[d]	20	2	45[e]
11[b]	(*o*-S$_2$C$_6$H$_4$) (**3**)	MeCN	50	10	63
12[b]	(H; SPh) (**2**)	THF	50	10	18
13	(SPh; SPh; H)[f] (**12**)	THF	20	20	42
14[b]	(I; I) (**9**)	THF	50	10	27

Conditions: *N*-benzylideneaniline (1.00 mmol), catalyst (10 μmol), solvent (5 cm^3), and H_2 (1 atm).[a] Yields of *N*-benzylaniline determined by GLC analyses. [b] No reaction at 20 °C. [c] Reached 80% after 20 h. [d] One mmol of MeCN was added. [e] Reached 97% after 48 h. [f] A combination of [Et_3NH]**12** and an equimolar amount of [Et_2OH][BF$_4$] was used as catalyst.

hardly proceeds in benzene (entry 3). A decrease of the reaction rate in benzene is also observed in catalysis by **3** (entry 9). Such solvent effect cannot be seen in hydrogenation of styrene (Table 1, entries 2–4). The activity of **3** is also lowered by addition of MeCN or by conducting the reaction in MeCN medium (entries 10, 11), probably because of difficulties in generating a vacant site for activating H_2. To achieve conditions without any MeCN molecules, the preparation of a catalyst from $[Et_3NH]$**12** and an equimolar amount of $[Et_2OH][BF_4]$ has been attempted, and this has resulted in higher conversion of *N*-benzylideneaniline than **1** as expected (entry 13 *vs.* 1).

In contrast to the relatively high activity toward the C=N bond, none of the chalcogenolato complexes in this study hydrogenates the more polarized C=O bonds in *e.g.* benzaldehyde and acetophenone under 1 atm H_2. Many molecular catalysts which heterolytically activate H_2 have already been reported, and these are generally effective in the hydrogenation of C=O bonds. Preferential hydrogenation of the C=N bond over C=O has rarely been found regardless of the operating mechanisms.[24,25] In the transfer hydrogenation using formic acid, NEt_3, and the bifunctional Ru catalyst developed by Noyori group, the imine is >1000 times more reactive than the ketone.[25a] According to Casey and co-workers,[26] the Shvo's complex $[(\eta^5\text{-}C_5Ph_4OH)Ru(CO)_2H]$, which is known to catalyze H_2- and transfer-hydrogenation of C=O bonds,[27] transfers H^+ and H^- to PhCH=NMe 26 times faster than to PhCHO in a stoichiometric reaction.

Two representative mechanisms involving heterolytic activation of H_2 have been proposed for catalytic hydrogenation. One, which is specific for metal–ligand bifunctional catalysts, is the concerted transfer of hydride and proton from the M(H)–E(H) moiety to a polar C=X bond (X = O, N).[3] The monothiolate complexes $[Cp^*M(PMe_3)(SDmp)][BAr^F{}_4]$ (M = Rh, Ir) recently reported by Ohki, Tatsumi *et al.* are suggested to operate in this manner *via* the active intermediates $[Cp^*MH(PMe_3)(HSDmp)][BAr^F{}_4]$ and hydrogenate both C=O and C=N bonds.[12b] The other route, in which proton and hydride are transferred separately and stepwise to the substrate, is called ionic mechanism.[2,28] To explain the features of catalysis, this mechanism seems plausible for hydrogenation of imine by the chalcogenolato complexes in this study. As in the cycle illustrated in Scheme 3, the chalcogenolato complexes **1**, **3**, or **4** form an adduct with H_2, from which H^+ is shifted to the imine (directly or mediated by any present bases). The resulting anionic hydrido complex transfers H^- to this iminium cation to produce an amine. Such a reaction pathway mediated by formation of active iminium has been proposed for other catalysts.[26,29] The lowest catalytic activity of **1** arises from the finding that **1** is converted easily to **2**, which is not included in the catalytic cycle. Thus, when hydrogenation of *N*-benzylideneaniline by **1** at 20 °C was monitored by NMR spectroscopy, hydrogenation gradually slowed down as the amount of **2** increased and finally stopped when **1** almost disappeared. Since such deactivation is suppressed by the use of the bidentate bdt ligand, **3** is the superior catalyst among them.[30] The dependence of the catalytic rate on solvents is in the order: benzene < THF < EtOH, probably because a polar solvent assists in the formation of ionic intermediates. The H_2-added complex is not acidic enough to protonate C=O (*vide supra*), and the anionic hydrido complex is presumably unable to reduce the non-activated C=O bond.



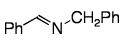
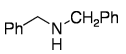
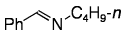
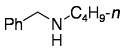
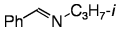
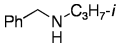
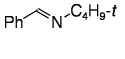
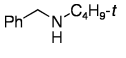
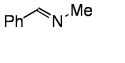
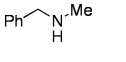
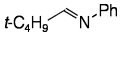
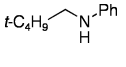
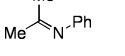
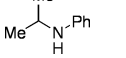
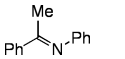
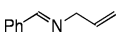
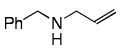
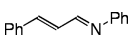
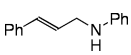
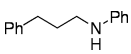
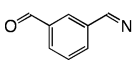
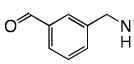
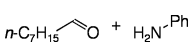
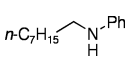
Scheme 3

Catalytic activities of **7** and **8** toward various unsaturated organic substrates were also examined at 1 atm, but only the latter could hydrogenate a stoichiometric amount of *N*-benzylideneaniline. The displacement of Tp^{Me2} by other isoelectronic co-ligands was attempted to some extent. The hydrotris(pyrazolyl) borate (Tp) complex $[TpRh(SC_6H_4Me\text{-}p)_2(MeCN)]$[15a] showed a low activity for hydrogenation of *N*-benzylideneaniline (1 atm, 50 °C, 50 h, TON = 16) and it was found to be inert for the C=C and C=O reductions. The related complex having a cyclopentadienyl ligand [Cp*Rh(bdt)],[31] which is known to exist in equilibrium with its dimer, has exhibited no activity of hydrogenation. These Cp* complexes did not exhibit any interaction with H_2 under 1 atm, regardless of the amine additives. Because the Cp* ligand is known to be more electron-donating than the Tp^{Me2} ligand in the case of Group 9 metal complexes,[15a,32] the Rh center of the non-ionic Cp* complex may not be acidic enough to activate H_2 heterolytically.

As a conclusion, it has been revealed that **3** is an excellent catalyst, which can chemoselectively hydrogenate imines under ambient temperature and pressure. As summarized in Table 3, the C=N bonds in various imines are efficiently hydrogenated under ambient temperature and pressure. While the size of the substituent on the N atom does not affect the reactivity so much, bulkiness of the groups attached to the imine carbon retards the reaction. *N*-(2,2-dimethylpropylidene) and *N*-(1-methylethylidene) derivatives were hydrogenated more slowly than *N*-benzylideneamines (entries 6 and 7 *vs.* 1–4), but *N*-(1-phenylethylidene)aniline could not be reduced even at 50 °C (entry 8). The conversion of *N*-benzylidenemethylamine was unexpectedly low, probably because the catalyst was deactivated by forming stable adducts, whose presence was detected by NMR (entry 5).

The C=C or C=O functions present in the substrate molecules are preserved (entries 9–11). However, the C=C bond conjugated with the C=N group was partially hydrogenated (entry 10), which probably proceeds *via* 1,4-addition, because allylamine is not susceptible to hydrogenation under these conditions. The amount of the saturated amine became smaller when EtOH was used instead of THF as a solvent. By virtue of inertness to C=O bonds, reductive amination[33] can be performed by mixing an aldehyde and a primary amine directly under hydrogenation conditions (entry 12).

Table 3 Hydrogenation of various imines catalyzed by **3**

entry	substrate	product	(yield/time)
1			(97%[a]/1 h)
2			(100%[b]/2 h)
3			(98%[b]/1 h)
4			(100%[b]/3 h)
5[c]			(4%[b,d]/10 h)
6[e]			(73%[f]/20 h)
7[e]			(91%[b]/20 h)
8[c]		no reaction	
9			(90%, [a]67%[f]/1 h)
10			(82%[a]/1 h) (88%[a]/3 h)[g]
			(15%[a]/1 h) (4%[a]/3 h)[g]
11			(99%[f]/1 h)
12[e]			(61%[f]/1 h)

Conditions: substrate (1.00 mmol) and **3** (10 μmol) in THF (5 cm^3) under 1 atm H_2 at 20 °C.[a] Determined by NMR. [b] Determined by GLC analyses. [c] Conducted at 50 °C. [d] Imine was recovered in 90%. [e] Conducted with 20 μmol catalyst loading. [f] Isolated yield. [g] Ethanol was used instead of THF.

Experimental

General

All manipulations were performed using standard Schlenk techniques under 1 atm of nitrogen or hydrogen atmosphere. Solvents were dried by common procedures and distilled under nitrogen before use. Complexes **1**,[15a] **4**, **5**,[15b] and **6**[21] were synthesized according to the literature methods. Imines *N*-(benzylidene)butylamine,[34] *N*-(2,2-dimethylpropylidene)-aniline,[35] *N*-(1-methylethylidene)aniline,[36] and *N*-(1-pheyl-ethylidene)aniline[37] were prepared from the corresponding amines and aldehydes or ketones. Some other organic compounds have been previously reported in the preceding communication.[16] Other reagents were commercially available and used as received.

NMR spectra (^1H at 400 MHz and ^{13}C at 100.5 MHz) were recorded on a JEOL alpha-400 spectrometer, and chemical shifts were referenced using those of residual solvent resonances (C_6D_6 at δ_H 7.15 ppm, THF-d_8 at δ_H 3.58, CD_3CN at δ_H 1.93, and $CDCl_3$ at δ_H 7.26 and δ_C 77.00). Sample solutions were made under a nitrogen atmosphere and measured at 20 °C unless otherwise specified. IR spectra were recorded on a JASCO FT/IR-420 spectrometer. Elemental analyses were done using a Perkin-Elmer 2400 series II CHN analyzer. GC and GC-MS analyses were performed by using Shimadzu GC-14B gas chromatographs and a GC-MS QP-5050 spectrometer equipped with a CBP 1 or CBP 10 fused silica capillary column (25 m × 0.25 mm ϕ).

Preparation of [Tp^{Me2}Rh(bdt)(MeCN)] (3). To a THF (50 cm^3) solution of **6** (646 mg, 1.17 mmol) was added 1,2-benzenedithiol (135 mm^3, 1.17 mmol) at 0 °C under a N_2 atmosphere. The yellow solution immediately turned to dark brown, and gas evolution was observed. After stirring for 5 min, the solvent was slowly evaporated under reduced pressure at 0 °C until the volume of the solution was reduced to 10 cm^3. Hexane (65 cm^3) was layered on the resulting brownish purple solution, and the mixture was left standing for 2 weeks at –20 °C. The liquid phase was discarded, and a powdery material was removed from the deposited solid by decantation and washing with hexane. The remaining claret crystals were dried under vacuum (493 mg, 61% yield as **3**·1.5THF). The crystals thus obtained were polymorphic, and two crystal systems containing one and two equivalents of THF molecules were confirmed by X-ray analyses. The amount of THF solvate molecules in bulk solid was determined by NMR measurement to be ~1.5 equiv. Anal. Calcd for $C_{29}H_{41}BN_7O_{1.5}RhS_2$: C, 50.51; H, 5.99; N, 14.22%. Found: C, 50.41; H, 6.14; N, 13.90%. ^1H NMR (C_6D_6): δ 0.22 (s, 3H, MeCN), 2.07, 2.81 (br, 9H each, Me in Tp^{Me2}), 5.34 (br, 1H, CH in Tp^{Me2}), 5.63 (br, 2H, CH in Tp^{Me2}), 6.96, 7.80 (dd, J_{HH} = 6.0, 3.2 Hz, 2H each, C_6H_4), 1.40, 3.57 (m, 6H each, THF). ^1H NMR (THF-d_8, –20 °C): δ 2.32, 2.34, 2.42 (s, 3H each, Me in Tp* and MeCN), 2.40, 2.68 (s, 6H each, Me in Tp^{Me2}), 5.65 (s, 1H, CH in Tp^{Me2}), 5.85 (s, 2H, CH in Tp^{Me2}), 6.61, 7.05 (dd, J_{HH} = 6.0, 3.2 Hz, 2H each, C_6H_4). ^1H NMR (CD_3CN): δ 2.20, 2.36 (br, 3H each, Me Tp^{Me2}), 2.40, 2.63 (br, 6H each, Me Tp^{Me2}), 5.72 (s, 1H, CH in Tp^{Me2}), 5.93 (s, 2H, CH in Tp^{Me2}), 6.74, 7.11 (dd, J_{H-H} = 5.9, 3.3 Hz, 2H each, C_6H_4). IR (KBr): 2530 (ν_{B-H}), 2323 ($\nu_{C\equiv N}$) cm^{-1}.

Preparation of [Tp^{Me2}RhH($SCH_2C_6H_2Me_2CH_2SH$-κ²*S*,*S*′)] (7). A mixture of **6** (861 mg, 1.56 mmol), 4,5-bis(mercaptomethyl)-*o*-xylene (310 mg, 1.56 mmol), and THF (10 cm^3) was stirred at room temperature under a N_2 atmosphere for 17 h. A deposited yellow solid was filtered off, washed with a small amount of THF, and dried under vacuum to yield **7** (158 mg). Addition of hexane to the above filtrate afforded the second crop as yellow microcrystals (331 mg, totally 52% yield). Anal. Calcd for $C_{25}H_{36}BN_6RhS_2$: C, 50.18; H, 6.06; N, 14.04%. Found: C, 50.08; H, 6.17; N, 13.79%. ^1H NMR (C_6D_6, 50 °C): δ –15.62 (d, J_{RhH} = 8.0 Hz, 1H, RhH), 2.05, 2.12 (s, 6H each, Me in Tp^{Me2} or $C_6H_2Me_2$), 2.25 (s, 3H, Me in Tp^{Me2}), 2.38 (br, 6H, Me in Tp^{Me2} or $C_6H_2Me_2$), 2.82 (br, 3H, Me in Tp^{Me2}), 3.28 (br, 1H, SH), 3.5–3.65 (m, 2H, SCH_2), 3.88 (d, J_{H-H} = 12.4 Hz, 2H, SCH_2), 5.51 (s, 2H, CH in Tp^{Me2}), 5.67 (s, 1H, CH in Tp^{Me2}), 6.77 (br, 2H, C_6H_2). IR (KBr): 2512 (ν_{B-H}), 2102 (ν_{Rh-H}) cm^{-1}.

Preparation of [Tp^{Me2}RhH(SC_6H_4-2-COOH-κ²*O*,*S*)] (8). Thiosalicylic acid (174 mg, 1.13 mmol) and **6** (620 mg, 1.12 mmol) were dissolved together in THF (10 cm^3) at 0 °C while stirring

under N_2. The resulting orange solution was filtered after 1 h, and hexane was layered on the concentrated filtrate. After storing at −20 °C for 1 week, an orange precipitate was filtered off, washed with hexane, and dried under vacuum to give **8**·THF (556 mg). The second crop was obtained from the mother liquor by crystallization from THF–hexane (39 mg, totally 84% yield). Anal. Calcd for $C_{26}H_{36}BN_6O_3RhS$: C, 49.85; H, 5.79; N, 13.42%. Found: C, 50.01; H, 5.94; N, 13.28%. ^{1}H NMR (C_6D_6): δ −13.79 (d, J_{RhH} = 11.6 Hz, 1H, RhH), 2.08, 2.19, 2.26, 2.31, 2.46, 2.79 (s, 3H each, Me in Tp^{Me2}), 5.40, 5.61, 5.77 (s, 1H each, CH in Tp^{Me2}), 6.60 (ddd, J_{HH} = 8.2, 6.8, 1.2 Hz, 1H, 4- or 5-H in C_6H_4), 6.78 (ddd, J_{HH} = 8.2, 6.8, 1.2 Hz, 1H, 4- or 5-H in C_6H_4), 7.96 (dd, J_{HH} = 8.2, 1.2 Hz, 1H, 3- or 6-H in C_6H_4), 8.01 (dd, J_{HH} = 8.2, 1.2 Hz, 1H, 3- or 6-H in C_6H_4), 9.13 (br, 1H, OH), 1.40, 3.57 (m, 4H each, THF). IR (KBr): 2523 (ν_{B-H}), 2057 (ν_{Rh-H}) 1617 ($\nu_{C=O}$) cm^{-1}.

Preparation of [$Tp^{Me2}RhI_2$(MeCN)] (9). A mixture of **6** (270 mg, 0.490 mmol) and I_2 (125 mg, 0.492 mmol) in THF (10 cm^3) was stirred under a N_2 atmosphere at room temperature overnight. The resulting reddish brown solution was filtered and concentrated to 8 cm^3. Addition of hexane (40 cm^3) yielded brown crystals (three polymorphs were found), which were filtered off and dried *in vacuo* (288 mg, 84% yield). Anal. Calcd for $C_{17}H_{25}BI_2N_7RhS_2$: C, 29.38; H, 3.63; N, 14.11%. Found: C, 29.72; H, 3.62; N, 13.70%. ^{1}H NMR (C_6D_6): δ 0.60 (s, 3H, MeCN), 2.04, 2.73 (s, 6H each, Me in Tp^{Me2}), 2.05, 3.36 (s, 3H each, Me in Tp^{Me2}), 5.49 (s, 1H, CH in Tp^{Me2}), 5.58 (s, 2H, CH in Tp^{Me2}). IR (KBr): 2526 (ν_{B-H}), 2330 ($\nu_{C\equiv N}$) cm^{-1}.

Preparation of [Tp^{Me2}RhH(SPh)(MeCN)] (2). Complex **1** (69 mg, 0.11 mmol) was dissolved in THF (5 mL) under a N_2 atmosphere, and the resulting solution was concentrated to 2 mL under reduced pressure. Then, H_2 gas was introduced, and the solution was allowed to stand at room temperature for 5 h. During this time, the color of the solution turned from red to reddish orange. After layering hexane (18 mL), the mixture was kept at −20 °C for 2 weeks. Deposited crystals were filtered off and dried in a stream of H_2. Lemon yellow prismatic crystals of **2**·2THF (47 mg, 64% yield) were manually separated from a small amount of red microcrystals of **1**. For use in the determination of the catalytic activity, this crop was further purified by repeating the above procedure another time. Anal. Calcd for $C_{31}H_{47}BN_7O_2RhS$: C, 53.53; H, 6.81; N, 14.10. Found: C, 53.83; H, 6.74; N, 14.63%. ^{1}H NMR (C_6D_6): δ −13.80 (d, J_{RhH} = 11.6 Hz, 1H, Rh–H), 0.35 (s, 3H, MeCN), 2.08, 2.15, 2.31, 2.32, 2.72, 2.84 (s, 3H each, Me in Tp^{Me2}), 5.42, 5.64, 5.86 (s, 1H each, CH in Tp^{Me2}), 6.95 (tt, J_{HH} = 7.2, 1.2 Hz, 1H, *p*-H in Ph), 7.15 (overlapping with C_6HD_5, *m*-H in Ph), 8.15 (dd, J_{HH} = 8.4, 1.2 Hz, 2H, *o*-H in Ph), 1.40, 3.57 (m, 8H each, THF). ^{1}H NMR (THF-d_8): δ −14.46 (d, J_{RhH} = 10.8 Hz, 1H, Rh–H), 2.20, 2.32, 2.33, 2.337, 2.342, 2.44, 2.56 (s, 3H each, Me in Tp^{Me2} and MeCN), 5.61, 5.73, 5.76 (s, 1H each, CH in Tp^{Me2}), 6.69 (m, 1H, *p*-H in Ph), 6.86 (t, J_{HH} = 7.6 Hz, 2H, *m*-H in Ph), 7.55 (d, J_{HH} = 7.6 Hz, 2H, *o*-H in Ph). IR (KBr): 2523 (ν_{B-H}), 2332 ($\nu_{C\equiv N}$), 2067 (ν_{Rh-H}) cm^{-1}.

^{1}H NMR studies under H_2. A representative procedure is as follows. Complex **1** (20 mg, 0.030 mmol) was dissolved in THF-d_8 (3.0 cm^3) under a N_2 atmosphere (if necessary, additives were mixed at this point). This solution was degassed by freeze-pump-saw cycles and stirred under a H_2 atmosphere at 20 °C. A part of the solution was periodically (30–60 min intervals) taken out and analyzed by NMR spectroscopy until the conversion reached a steady state. After 1 h, an equilibrium mixture of **1**, **2**, and PhSH in a 1 : 14 : 14 ratio was observed. This solution was then degassed by freeze-pump-saw cycles and kept under a N_2 atmosphere for 40 h. NMR measurements of the resulting solution confirmed that the ratio of **1**, **2**, and PhSH became 1 : 0.32 : 0.31, and it changed to 1 : 0.21 : 0.21 after further 26 h. Data for the complexes characterized by ^{1}H NMR in these experiments are listed below.

[Tp^{Me2}RhH(SePh)(MeCN)] (10). δ(C_6D_6) = −14.05 (d, J_{RhH} = 10.4 Hz, 1H, Rh–H), 0.39 (s, 3H, MeCN), 2.09, 2.15, 2.30, 2.32, 2.80, 2.86 (s, 3H each, Me in Tp^{Me2}), 5.44, 5.64, 5.86 (s, 1H each, CH in Tp^{Me2}), 8.2–8.25 (m, 2H, *o*-H in Ph). δ(THF-d_8) = −14.70 (d, J_{RhH} = 10.8 Hz, 1H, Rh–H), 2.319, 2.324, 2.33, 2.41, 2.60 (s, 3H each, Me in MeCN or Tp^{Me2}, other two Me signals could not be assigned due to overlapping with those of other species), 5.62, 5.72, 5.76 (s, 1H each, CH in Tp^{Me2}), 6.8–6.9 (m, 3H, *m*-, and *p*-H in Ph), 7.65–7.7 (m, 2H, *o*-H in Ph).

[DMAN·H][Tp^{Me2}RhH($SePh)_2$] ([DMAN·H]13). δ(THF-d_8) = −16.48 (d, J_{RhH} = 8.8 Hz, 1H, Rh–H), 5.38 (s, 2H, CH in Tp^{Me2}), 5.60 (s, 1H, CH in Tp^{Me2}), 6.45–6.55 (m, 6H, *m*-, and *p*-H in Ph), 7.25 (d, J_{H-H} = 7.6 Hz, 4H, *o*-H in Ph).

[DMAN·H][Tp^{Me2}Rh($SePh)_3$] ([DMAN·H]14). δ(THF-d_8) = 5.31 (s, 3H, CH in Tp^{Me2}), 6.35 (t, J_{HH} = 7.6 Hz, 6H, *m*-H in Ph), 6.48 (t, J_{HH} = 7.6 Hz, 3H, *p*-H in Ph), 6.54 (d, J_{HH} = 7.6 Hz, 6H, *o*-H in Ph).

Assignment of Me groups in above two complexes was hampered by severe overlapping of both signals. Signals of [DMAN·H]$^+$ were as follows: δ(THF-d_8) = 3.25 (d, J_{HH} = 2.8 Hz, 12H), 7.67 (t, J_{HH} = 8.0 Hz, 2H), 8.00, 8.04 (d, J_{HH} = 8.0 Hz, 2H each).

[DMAN·H][Tp^{Me2}RhH(bdt)] ([DMAN·H]11). δ(THF-d_8) = −18.75 (d, J_{RhH} = 15.2 Hz, 1H, Rh–H), 2.12, 2.36 (s, 3H each, Me in Tp^{Me2}), 2.31, 2.45 (s, 6H each, Me in Tp^{Me2}), 3.00 (br, 12H, NMe_2), 5.48 (s, 1H, CH in Tp^{Me2}), 5.57 (s, 2H, CH in Tp^{Me2}), 6.34, 7.04 (dd, J_{HH} = 5.6, 3.2 Hz, 2H each, C_6H_4), 7.67 (t, J_{H-H} = 7.6 Hz, 2H, aromatic H in DMAN·H$^+$) 7.9–8.0 (m, 4H, aromatic H in DMAN·H$^+$). δ(CD_3CN) = −18.89 (d, J_{RhH} = 15.2 Hz, 1H, Rh–H), 2.05, 2.38 (s, 3H each, Me in Tp^{Me2}), 2.33, 2.42 (s, 6H each, Me in Tp^{Me2}), 5.60 (s, 1H, CH in Tp^{Me2}), 5.70 (s, 2H, CH in Tp^{Me2}), 6.45, 6.95 (dd, J_{HH} = 6.0, 3.2 Hz, 2H each, C_6H_4).

[Bu_3NH][Tp^{Me2}RhH(bdt)] ([Bu_3NH]11). δ(THF-d_8) = −18.76 (d, J_{RhH} = 14.4 Hz, 1H, Rh–H), 1.97, 2.37 (s, 3H each, Me in Tp^{Me2}), 2.33, 2.43 (s, 6H each, Me in Tp^{Me2}), 5.56 (s, 1H, CH in Tp^{Me2}), 5.65 (s, 2H, CH in Tp^{Me2}), 6.46, 7.04 (dd, J_{HH} = 5.8, 3.4 Hz, 2H each, C_6H_4). Signals of Bu_3NH^+ were merged with those of free Bu_3N.

Preparation of [Et_3NH][Tp^{Me2}RhH(bdt)] ([Et_3NH]11)

To a solution of **3**·1.5THF (62 mg, 0.090 mmol) in THF (5 cm^3), NEt_3 (45 μL, 0.32 mmol) was added and the mixture was stirred at room temperature under H_2. The purple solution turned pale yellow-brown within 5 min, and a off-white solid started to deposit after 10 min. After stirring the mixture for 1 h, a solid was filtered off, washed with a small amount of THF, and dried under vacuum

(33 mg, 56% yield). Anal. Calcd for $C_{27}H_{43}BN_7RhS_2$: C, 50.39; H, 6.73; N, 15.24. Found: C, 50.66; H, 6.75; N, 15.23%. ^{1}H NMR (CD_3CN): δ −18.90 (d, J_{RhH} = 14.8 Hz, 1H, RhH), 1.16 (t, J_{HH} = 7.2 Hz, 9H, NCH_2CH_3), 2.04, 2.38 (s, 3H each, Me in Tp^{Me2}), 2.34, 2.42 (s, 6H each, Me in Tp^{Me2}), 2.98 (q, J_{HH} = 7.2 Hz, 6H, NCH_2CH_3), 5.61 (s, 1H, CH in Tp^{Me2}), 5.71 (s, 2H, CH in Tp^{Me2}), 6.47, 6.96 (dd, J_{HH} = 5.7, 3.3 Hz, 2H each, C_6H_4). IR (KBr): 2670 (ν_{N-H}), 2508 (ν_{B-H}), 2104, 2072$_{sh}$ (ν_{Rh-H}) cm^{-1}.

Preparation of [Et$_3$NH][Tp^{Me2}RhH(SPh)$_2$] ([Et$_3$NH]12)

Immediately (<5 min) after dissolving **1** (65 mg, 0.099 mmol) in THF (4.5 cm^3) under H_2 at room temperature, NEt_3 (42 μL, 0.30 mmol) was added to this solution. A pale orange solution was obtained after stirring for 3 h, and it was dried up under reduced pressure, leaving a yellow crystalline solid. This was washed with benzene (5 cm^3) and dried under vacuum (34 mg, 47% yield). Anal. Calcd for $C_{33}H_{49}BN_7RhS_2$: C, 54.92; H, 6.84; N, 13.59. Found: C, 55.50; H, 6.99; N, 13.53%. ^{1}H NMR (CD_3CN): δ −15.93 (d, J_{RhH} = 10.8 Hz, 1H, RhH), 1.18 (t, J_{HH} = 7.2 Hz, 9H, NCH_2CH_3), 2.20, 2.35 (s, 6H each, Me in Tp^{Me2}), 2.47, 2.49 (s, 3H each, Me in Tp^{Me2}), 3.02 (q, J_{HH} = 7.2 Hz, 6H, NCH_2CH_3), 5.54 (s, 2H, CH in Tp^{Me2}), 5.67 (s, 1H, CH in Tp^{Me2}), 6.50–6.55 (m, 2H, *p*-H in Ph), 6.61–6.66 (m, 4H, *m*-H in Ph), 7.01–7.04 (m, 4H, *o*-H in Ph). IR (KBr): 2656 (ν_{N-H}), 2519 (ν_{B-H}), 2084 (ν_{Rh-H}) cm^{-1}.

Catalytic hydrogenation

A standard method of the hydrogenation is as follows. The substrate organic compound (1.00 mmol) was dissolved in THF (5 cm^3), and the solution was degassed by freeze-pump-saw cycles. Hydrogen gas was introduced to the reaction vessel, and the catalyst complex (0.010 mmol) was added. The solution was stirred under 1 atm of H_2, and other conditions were set as described in Tables 1–3. The reaction mixtures were analyzed by GLC or NMR methods after addition of internal standards or worked up for isolation of the products. Compounds which have not been reported in previous report[16] and whose authentic samples are not commercially available are listed below.

***N*-neopentylaniline[38].** A pale yellow oil was obtained in 74% yield by column chromatography on silica gel eluting with CH_2Cl_2–MeOH (9/1). ^{1}H NMR ($CDCl_3$): δ 0.99 (s, 9H, CH_3), 2.89 (br, 2H, NCH_2), 3.62 (br, 1H, NH), 6.62 (d, J_{HH} = 8.8 Hz, 2H, *o*-H in Ph), 6.66 (t, J_{HH} = 7.4 Hz, 1H, *p*-H in Ph), 7.1–7.2 (m, 2H, *m*-H in Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.7, 31.9, 55.8, 112.5, 116.8, 129.1, 149.0.

***N*-benzylallylamine.** A colorless oil was isolated in 67% yield by column chromatography on silica gel eluting with CH_2Cl_2–MeOH (9/1). NMR data were in good agreement with the literature values.[39]

Crystallographic study of 3·2THF, 3·THF, 8·THF, and 9·THF

X-Ray diffraction studies were done on a Rigaku Mercury-CCD diffractometer equipped with a graphite monochromatized Mo-Kα source (λ = 0.71071 Å) by using the CrystalClear program package.[40] All data were corrected for Lorentz and polarization effects as well as for absorption. Structure solution and refinement were carried out by using the CrystalStructure program package.[41] All unique data within the limits of $6° < 2\theta < 55°$ were used. The positions of the non-hydrogen atoms were determined by Patterson methods (PATTY[42]) for **3** and **9** or direct method (SHELXS97[43]) for **8** and subsequent Fourier synthesis (DIRDIF99[44]), and they were refined with anisotropic thermal parameters by full-matrix least-squares techniques. Hydrogen atoms of the complex molecules in **3**·2THF were found from difference Fourier map and refined isotropically, while those in **3**·THF and **9**·THF were placed at the calculated positions. For **8**·THF, all hydrogen atoms of complex and THF molecules were positioned by means of difference Fourier map and isotropically refined. Hydrogen atoms of other solvating THF molecules were placed according to geometry except for those in the disordered ones.

Crystal data of 3·2THF

$C_{31}H_{45}BN_7O_2RhS_2$, M = 725.58, monoclinic, a = 10.180(2), b = 22.607(4), c = 14.737(2) Å, β = 91.2870(7)°, U = 3390.8(9) Å^3, T = 113 K, space group $P2_1/c$ (no. 14), Z = 4, 35590 reflections measured, 8065 unique (R_{int} = 0.029) which were used in all calculations. The final $wR(F^2)$ was 0.123 (all data).

Crystal data of 3·THF

$C_{27}H_{37}BN_7ORhS_2$, M = 653.47, monoclinic, a = 10.248(2), b = 19.925(4), c = 15.443(3) Å, β = 101.7510(7)°, U = 3087(1) Å^3, T = 293 K, space group $P2_1/n$ (no. 14), Z = 4, 24530 reflections measured, 7041 unique (R_{int} = 0.023) which were used in all calculations. The final $wR(F^2)$ was 0.111 (all data).

Crystal data of 8·THF

$C_{26}H_{36}BN_6O_3RhS$, M = 626.38, monoclinic, a = 10.137(2), b = 18.086(3), c = 15.833(3) Å, β = 102.7935(8)°, U = 2831(1) Å^3, T = 113 K, space group $P2_1/c$ (no. 14), Z = 4, 22692 reflections measured, 6749 unique (R_{int} = 0.030) which were used in all calculations. The final $wR(F^2)$ was 0.053 (all data).

Crystal data of 9·THF

$C_{21}H_{33}BI_2N_7ORh$, M = 767.06, monoclinic, a = 7.978(2), b = 13.431(3), c = 26.285(5) Å, β = 97.916(3)°, U = 2789.8(9) Å^3, T = 113 K, space group $P2_1/c$ (no. 14), Z = 4, 33333 reflections measured, 6664 unique (R_{int} = 0.036) which were used in all calculations. The final $wR(F^2)$ was 0.117 (all data).

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References

1 (*a*) P. J. Brothers, *Prog. Inorg. Chem.*, 1981, **28**, 1–61; (*b*) R. H. Morris, *Can. J. Chem.*, 1996, **74**, 1907–1915; (*c*) G. J. Kubas, *Adv. Inorg. Chem.*, 2004, **56**, 127–177; (*d*) G. J. Kubas, *Catal. Lett.*, 2005, **104**, 79–101.

2 (*a*) H. Jacobsen and H. Berke, in *Recent Advances in Hydride Chemistry*, ed. M. Peruzzini and R. Poli, Elsevier Science B.V., Amsterdam, 2001, pp 89-116; (*b*) R. M. Bullock, *Chem.–Eur. J.*, 2004, **10**, 2366–2374.

3 Recent reviews: (*a*) R. Noyori and T. Ohkuma, *Angew. Chem., Int. Ed.*, 2001, **40**, 40–73; (*b*) S. E. Clapham, A. Hadzovic and R. H. Morris, *Coord. Chem. Rev.*, 2004, **248**, 2201–2237; (*c*) T. Ikariya, K. Murata and R. Noyori, *Org. Biomol. Chem.*, 2006, **4**, 393–406; (*d*) M. Ito and T. Ikariya, *Chem. Commun.*, 2007, 5134–5142.

4 Recent reviews: (*a*) P. M. Vignais and B. Billoud, *Chem. Rev.*, 2007, **107**, 4206–4272; (*b*) J. C. Fontecilla-Camps, A. Volbeda, C. Cavazza and Y. Nicolet, *Chem. Rev.*, 2007, **107**, 4273–4303; (*c*) A. L. De Lacey, V. M. Fernández, M. Rousset and R. Cammack, *Chem. Rev.*, 2007, **107**, 4304–4330; (*d*) W. Lubitz, E. Reijerse and M. van Gastel, *Chem. Rev.*, 2007, **107**, 4331–4365; (*e*) K. A. Vincent, A. Parkin and F. A. Armstrong, *Chem. Rev.*, 2007, **107**, 4366–4413; (*f*) P. E. M. Siegbahn, J. W. Tye and M. B. Hall, *Chem. Rev.*, 2007, **107**, 4414–4435; (*g*) H. Ogata, W. Lubitz and Y. Higuchi, *Dalton Trans.*, 2009, 7577–7587; (*h*) J. C. Fontecilla-Camps, P. Amara, C. Cavazza, Y. Nicolet and A. Volbeda, *Nature*, 2009, **460**, 814–822.

5 Reviews on functional models: (*a*) I. P. Georgakaki, L. M. Thomson, E. J. Lyon, M. B. Hall and M. Y. Darensbourg, *Coord. Chem. Rev.*, 2003, **238–239**, 255–266; (*b*) C. Tard and C. J. Pickett, *Chem. Rev.*, 2009, **109**, 2245–2274; (*c*) F. Gloaguen and T. B. Rauchfuss, *Chem. Soc. Rev.*, 2009, **38**, 100–108; (*d*) S. Ogo, *Chem. Commun.*, 2009, 3317–3325; (*e*) J.-F. Capon, F. Gloaguen, F. Y. Pétillon, P. Schollhammer and J. Talarmin, *Coord. Chem. Rev.*, 2009, **253**, 1476–1494; (*f*) D. M. Heinkey, *J. Organomet. Chem.*, 2009, **694**, 2671–2680; (*g*) G. A. N. Felton, C. A. Mebi, B. J. Petro, A. K. Vannucci, D. H. Evans, R. S. Glass and D. L. Lichtenberger, *J. Organomet. Chem.*, 2009, **694**, 2681–2699.

6 (*a*) Y. Nicolet, A. L. de Lacey, X. Vernède, V. M. Fernandez, E. C. Hatchikian and J. C. Fontecilla-Camps, *J. Am. Chem. Soc.*, 2001, **123**, 1596–1601; (*b*) H.-J. Fan and M. B. Hall, *J. Am. Chem. Soc.*, 2001, **123**, 3828–3829; (*c*) H. X. Li and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 2002, **124**, 726–727; (*d*) J. L. Stanley, Z. M. Heiden, T. B. Rauchfuss, S. R. Wilson, L. De Gioia and G. Zampella, *Organometallics*, 2008, **27**, 119–125; (*e*) A. S. Pandey, T. V. Harris, L. J. Giles, J. W. Peters and R. K. Szilagyi, *J. Am. Chem. Soc.*, 2008, **130**, 4533–4540.

7 (*a*) L. De Gioia, P. Fantucci, B. Guigliarelli and P. Bertrand, *Inorg. Chem.*, 1999, **38**, 2658–2662; (*b*) S. Niu, L. M. Thomson and M. B. Hall, *J. Am. Chem. Soc.*, 1999, **121**, 4000–4007; (*c*) P. Amara, A. Volbeda, J. C. Fontecilla-Camps and M. J. Field, *J. Am. Chem. Soc.*, 1999, **121**, 4468–4477; (*d*) S. Niu and M. B. Hall, *Inorg. Chem.*, 2001, **40**, 6201–6203; (*e*) A. Pardo, A. L. de Lacey, V. M. Fernandez, H. J. Fan, Y. Fan and M. B. Hall, *JBIC, J. Biol. Inorg. Chem.*, 2006, **11**, 286–306.

8 (*a*) S. Shima and R. K. Thauer, *Chem. Rec.*, 2007, **7**, 37–46; (*b*) S. Shima, O. Pilak, S. Vogt, M. Schick, M. S. Stagni, W. Meyer-Klaucke, E. Warkentin, R. K. Thauer and U. Ermler, *Science*, 2008, **321**, 572–575; (*c*) T. Hiromoto, K. Ataka, O. Pilak, S. Vogt, M. S. Stagni, W. Meyer-Klaucke, E. Warkentin, R. K. Thauer, S. Shima and U. Ermler, *FEBS Lett.*, 2009, **583**, 585–590; (*d*) T. Hiromoto, E. Warkentin, J. Mol, U. Ermler and S. Shima, *Angew. Chem., Int. Ed.*, 2009, **48**, 6457–6460.

9 (*a*) X. Wang, Z. Li, X. Zeng, Q. Luo, D. J. Evans, C. J. Pickett and X. Liu, *Chem. Commun.*, 2008, 3555–3557; (*b*) X. Yang and M. B. Hall, *J. Am. Chem. Soc.*, 2008, **130**, 14036–14037; (*c*) A. M. Royer, T. B. Rauchfuss and D. L. Gray, *Organometallics*, 2009, **28**, 3618–3620; (*d*) X. Yang and M. B. Hall, *J. Am. Chem. Soc.*, 2009, **131**, 10901–10908; (*e*) N. Nakatani, Y. Nakao, H. Sato and S. Sakaki, *Chem. Lett.*, 2009, **38**, 958–959; (*f*) B. Li, T. Liu, C. V. Popescu, A. Bilko and M. Y. Darensbourg, *Inorg. Chem.*, 2009, **48**, 11283–11289.

10 (*a*) D. Sellmann, J. Käppler and M. Moll, *J. Am. Chem. Soc.*, 1993, **115**, 1830–1835; (*b*) P. G. Jessop and R. H. Morris, *Inorg. Chem.*, 1993, **32**, 2236–2237; (*c*) D. Sellmann, T. Gottschalk-Gaudig and F. W. Heinemann, *Inorg. Chem.*, 1998, **37**, 3982–3988; (*d*) D. Sellmann and A. Fürsattel, *Angew. Chem., Int. Ed.*, 1999, **38**, 2023–2026; (*e*) D. Sellmann, F. Geipel and M. Moll, *Angew. Chem., Int. Ed.*, 2000, **39**, 561–563; (*f*) D. Sellmann, R. Prakash, F. W. Heinemann, M. Moll and M. Klimowicz, *Angew. Chem., Int. Ed.*, 2004, **43**, 1877–1880; (*g*) T. Matsumoto, Y. Nakaya and K. Tatsumi, *Angew. Chem., Int. Ed.*, 2008, **47**, 1913–1915.

11 (*a*) M. Schlaf, A. J. Lough and R. H. Morris, *Organometallics*, 1996, **15**, 4423–4436; (*b*) D. Sellmann, G. H. Rackelmann and F. W. Heinemann, *Chem.–Eur. J.*, 1997, **3**, 2071–2079; (*c*) Y. Ohki, M. Sakamoto and K. Tatsumi, *J. Am. Chem. Soc.*, 2008, **130**, 11610–11611.

12 (*a*) Y. Ohki, Y. Takikawa, H. Sadohara, C. Kesenheimer, B. Engendahl, E. Kapatina and K. Tatsumi, *Chem.–Asian J.*, 2008, **3**, 1625–1635; (*b*) M. Sakamoto, Y. Ohki, G. Kehr, G. Erker and K. Tatsumi, *J. Organomet. Chem.*, 2009, **694**, 2820–2824.

13 (*a*) M. Rakowski DuBois, M. C. VanDerveer, D. L. DuBois, R. C. Haltiwanger and W. K. Miller, *J. Am. Chem. Soc.*, 1980, **102**, 7456–7461; (*b*) C. V. Laurie, L. Duncan, R. C. Haltiwanger, R. T. Weberg and M. Rakowski DuBois, *J. Am. Chem. Soc.*, 1986, **108**, 6234–6241; (*c*) C. Bianchini, C. Meali, A. Meli and M. Sabat, *Inorg. Chem.*, 1986, **25**, 4618–4618; (*d*) Z. K. Sweeney, J. L. Polse, R. A. Andersen, R. G. Bergman and M. G. Kubinec, *J. Am. Chem. Soc.*, 1997, **119**, 4543–4544; (*e*) Z. K. Sweeney, J. L. Polse, R. G. Bergman and R. A. Andersen, *Organometallics*, 1999, **18**, 5502–5510; (*f*) R. C. Linck, R. J. Pafford and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 2001, **123**, 8856–8857; (*g*) H. Kato, H. Seino, Y. Mizobe and M. Hidai, *J. Chem. Soc., Dalton Trans.*, 2002, 1494–1499; (*h*) Y. Ohki, N. Matsuura, T. Marumoto, H. Kawaguchi and K. Tatsumi, *J. Am. Chem. Soc.*, 2003, **125**, 7978–7988; (*i*) A. Ienco, M. J. Calhorda, J. Reinhold, F. Reineri, C. Bianchini, M. Peruzzini, F. Vizza and C. Mealli, *J. Am. Chem. Soc.*, 2004, **126**, 11954–11965.

14 (*a*) F. Takagi, H. Seino, Y. Mizobe and M. Hidai, *Can. J. Chem.*, 2001, **79**, 632–634; (*b*) F. Takagi, H. Seino, M. Hidai and Y. Mizobe, *J. Chem. Soc., Dalton Trans.*, 2002, 3603–3610; (*c*) F. Takagi, H. Seino, M. Hidai and Y. Mizobe, *Organometallics*, 2003, **22**, 1065–1071; (*d*) H. Kajitani, H. Seino and Y. Mizobe, *Organometallics*, 2005, **24**, 6260–6267; (*e*) A. Saito, H. Seino, H. Kajitani, F. Takagi, A. Yashiro, T. Ohnishi and Y. Mizobe, *J. Organomet. Chem.*, 2006, **691**, 5746–5752 .

15 (*a*) H. Seino, T. Yoshikawa, M. Hidai and Y. Mizobe, *Dalton Trans.*, 2004, 3593–3600; (*b*) S. Nagao, H. Seino, M. Hidai and Y. Mizobe, *Dalton Trans.*, 2005, 3166–3172; (*c*) Y. Misumi, H. Seino and Y. Mizobe, *J. Organomet. Chem.*, 2006, **691**, 3157–3164; (*d*) Y. Misumi, H. Seino and Y. Mizobe, *Inorg. Chim. Acta*, 2009, **362**, 4409–4415.

16 Y. Misumi, H. Seino and Y. Mizobe, *J. Am. Chem. Soc.*, 2009, **131**, 14636–14637.

17 Complex **7** was fairly stable at room temperature and converted by refluxing in THF to the product having one type of hydrido ligand. A structure of the dimer of **7** was suggested from the ^{1}H NMR pattern.

18 (*a*) W. Hieber and M. Gsheidmeier, *Chem. Ber.*, 1966, **99**, 2312–2321; (*b*) W. Henderson and B. K. Nicholson, *Inorg. Chim. Acta*, 2004, **357**, 2231–2236.

19 W. Hieber and W. Rohm, *Chem. Ber.*, 1969, **102**, 2787–2803.

20 (*a*) V. Circu, M. A. Fernandes and L. Carlton, *Inorg. Chem.*, 2002, **41**, 3859–3865; (*b*) C. Cao, T. Wang, B. O. Patrick and J. A. Love, *Organometallics*, 2006, **25**, 1321–1324.

21 K. Ohta, M. Hashimoto, Y. Takahashi, S. Hikichi, M. Akita and Y. Moro-oka, *Organometallics*, 1999, **18**, 3234–3240.

22 (*a*) K. Abdur-Rashid, T. P. Fong, B. Greaves, D. G. Gusev, J. G. Hinman, S. E. Landau, A. J. Lough and R. H. Morris, *J. Am. Chem. Soc.*, 2000, **122**, 9155–9171; (*b*) A. Streitwieser and Y.-J. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 11783–11786; (*c*) A. Macchioni, *Chem. Rev.*, 2005, **105**, 2039–2074; (*d*) G. Garrido, E. Koort, C. Ràfols, E. Bosch, T. Rodima, I. Leito and M. Rosés, *J. Org. Chem.*, 2006, **71**, 9062–9067.

23 S. May, P. Reinsalu and J. Powell, *Inorg. Chem.*, 1980, **19**, 1582–1589.

24 (*a*) Y. Ng Cheong Chan, D. Meyer and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1990, 869–871; (*b*) Y. Ng Cheong Chan and J. A. Osborn, *J. Am. Chem. Soc.*, 1990, **112**, 9400–9401; (*c*) T. Gross, A. M. Seayad, M. Ahmad and M. Beller, *Org. Lett.*, 2002, **4**, 2055–2058.

25 Under transfer hydrogenation conditions: (*a*) N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1996, **118**, 4916–4917; (*b*) S. Ogo, K. Uehara, T. Abura and S. Fukuzumi, *J. Am. Chem. Soc.*, 2004, **126**, 3020–3021.

26 C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi and M. Kavana, *J. Am. Chem. Soc.*, 2001, **123**, 1090–1100.

27 (*a*) Y. Shvo, D. Czarkie and Y. Rahamim, *J. Am. Chem. Soc.*, 1986, **108**, 7400–7402; (*b*) C. P. Casey, S. E. Beetner and J. B. Johnson, *J. Am. Chem. Soc.*, 2008, **130**, 2285–2295, and references therein.

28 (*a*) R. M. Bullock and M. H. Voges, *J. Am. Chem. Soc.*, 2000, **122**, 12594–12595; (*b*) M. P. Magee and J. R. Norton, *J. Am. Chem. Soc.*, 2001, **123**, 1778–1779; (*c*) M. H. Voges and R. M. Bullock, *J. Chem. Soc., Dalton Trans.*, 2002, 759–770; (*d*) H. Guan, M. Iimura, M. P. Magee, J. R. Norton and K. E. Janak, *Organometallics*, 2003, **22**, 4084–4089; (*e*) H. Guan, M. Iimura, M. P. Magee, J. R. Norton and G. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 7805–7814; (*f*) B. F. M. Kimmich, P. J. Fagan, E. Hauptman, W. J. Marshall and R. M. Bullock, *Organometallics*, 2005, **24**, 6220–6229; (*g*) S. Namorado, M. A. Antunes, L. F. Veiros, J. R. Ascenso, M. T. Duarte and A. M. Martins, *Organometallics*, 2008, **27**, 4589–4599.

29 (*a*) J. B. Åberg, J. S. M. Samec and J.-E. Bäckvall, *Chem. Commun.*, 2006, 2771–2773; (*b*) S. Shirai, H. Nara, Y. Kayaki and T. Ikariya, *Organometallics*, 2009, **28**, 802–809.
30 NMR measurements after the completion of catalysis confirmed that most of catalyst remained as **3** under the conditions of entry 8 in Table 2 (~ 1 h, ~ 100 TON).
31 R. Xi, M. Abe, T. Suzuki, T. Nishioka and K. Isobe, *J. Organomet. Chem.*, 1997, **549**, 117–125.
32 D. M. Tellers, S. J. Skoog, R. G. Bergman, T. B. Gunnoe and W. D. Harman, *Organometallics*, 2000, **19**, 2428–2432.
33 (*a*) V. I. Tararov, R. Kadyrov, T. H. Riermeier, U. Dingerdissen and A. Bömer, *Org. Prep. Proced. Int.*, 2004, **36**, 99–120; (*b*) S. Gomez, J. A. Peters and T. Maschmeyer, *Adv. Synth. Catal.*, 2002, **344**, 1037–1057.
34 K. N. Campbell, C. H. Helbing, M. P. Florkowski and B. K. Campbell, *J. Am. Chem. Soc.*, 1948, **70**, 3868–3870.
35 Q. F. Mokuolu, P. A. Duckmanton, P. B. Hitchcock, C. Wilson, A. J. Blake, L. Shukla and J. B. Love, *Dalton Trans.*, 2004, 1960–1970.
36 D. R. Eaton and J. P. K. Tong, *Inorg. Chem.*, 1980, **19**, 740–744.
37 P. Schnider, G. Koch, R. Prétôt, G. Wang, F. M. Bohnen, C. Krüger and A. Pfaltz, *Chem.–Eur. J.*, 1997, **3**, 887–892.
38 H. Sajiki, T. Ikawa and K. Hirota, *Org. Lett.*, 2004, **6**, 4977–4980.
39 J. Barluenga, R.-M. Canteli and J. Flórez, *J. Org. Chem.*, 1994, **59**, 602–606.
40 CrystalClear 1.3.6: Rigaku/MSC: 9009 New Trails Dr The Woodlands TX 77381, USA, (1998–2006).
41 CrystalStructure 3.8.0: *Crystal structure analysis package*, Rigaku and Rigaku/MSC: 9009 New Trails Dr The Woodlands TX 77381, USA (2000-2006). CRYSTALS Issue 11: J. R. Carruthers, J. S. Rollett, P. W. Betteridge, D. Kinna, L. Pearce, A. Larsen and E. Gabe, Chemical Crystallography Laboratory, Oxford, UK (1999).
42 PATTY: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykall, *The DIRDIF program system*, Technical Report of the Crystallography Laboratory: University of Nijmegen, The Netherlands, 1992.
43 SHELXS97: G. M. Sheldrick, *Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997.
44 DIRDIF99: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, *The DIRDIF-99 program system*, Technical Report of the Crystallography Laboratory: University of Nijmegen, The Netherlands, 1999.

